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Formation of Metalloheterocycles by Addition of Heteroallenes to the  
Electron-Rich Carbonyl Complex  $[W(\eta-C_5H_5)_2(CO)]$

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Abstract: The reactions of  $[W(\eta-C_5H_5)_2(CO)]$  (1) with a range of heteroallenes establish that 4-membered metalloheterocycles can be formed by addition of heteroallenes to an electron rich neutral carbonyl complex. Metallocycloimides  $[W(\eta-C_5H_5)_2\{C(O)N(R)C(O)\}]$  (2, R=CH<sub>3</sub>; 3, R=Ph) are formed by addition of methyl and phenyl isocyanate to 1, and the metallocycloacylamidine  $[W(\eta-C_5H_5)_2\{C(O)-N(Ph)C(NPh)\}]$  (4), is formed by addition of diphenylcarbodiimide to 1. In surprising contrast, addition of phenyl isothiocyanate to 1 leads to formation of a 4-membered metalloheterocycle determined by single crystal x-ray diffraction ( $R_w = 3.77\%$ ) to be the metallocyclothioacylamidine  $[W(\eta-C_5H_5)_2\{C(S)N(Ph)C(NPh)\}]$  (5). The complex crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 7.816$  (2),  $b = 19.838$  (5),  $c = 13.066$  (3) Å,  $\beta = 92.33$  (2)°,  $d_{calcd} = 1.81$  g mL<sup>-1</sup>,  $Z = 4$ . It is proposed that initial  $S=C=NPh$  addition to 1 results in ring closure through S to give a metallocycle which eliminates COS (GC) to form an intermediate isonitrile complex. Addition of a second  $S=C=NPh$  with ring closure through N then leads to 5. There is a fine balance between ring closure through S and N in isothiocyanate addition to 1, and  $S=C=NCH_3$  forms predominantly the metallocycloacylthioamide  $[W(\eta-C_5H_5)_2\{C(S)N(CH_3)C(O)\}]$  (8) in diethyl ether, and a mixture of 8 (53%) and the bis adduct  $[W(\eta-C_5H_5)_2\{C(NCH_3)N(CH_3)C(S)\}]$  (9) (27%) in pentane.

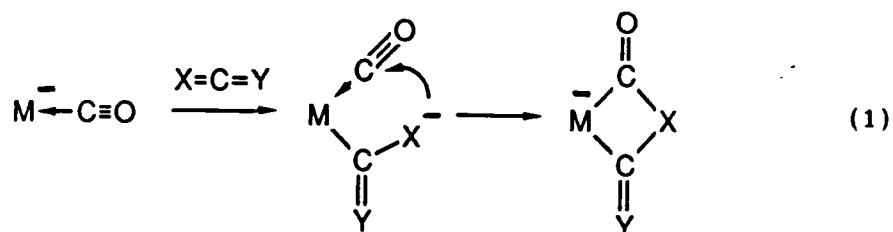
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## Introduction

It is now well established that coordination of heteroallenes to anionic transition metal complexes containing carbonyl ligands can result in incorporation of heteroallenes into metalloheterocycles as shown in Eq. 1. In the case of  $\text{CO}_2$ , for example, we have suggested that the accessibility of metalloanhydrides ( $X = Y = \text{O}$ ) is responsible for the facile scrambling of labeled oxygens between coordinated  $\text{CO}_2$  and coordinated CO in  $\eta^1\text{-C}$  complexes of  $\text{CO}_2$  with  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]^{-3}$  and  $[\text{W}(\text{CO})_5]^{2-}$ .<sup>4</sup> Fehlhammer and his coworkers have also established that metalloheterocycles are the ground state structures of complexes of salts of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO}_2)]^-$  with diimides ( $\text{RN}=\text{C}=\text{NR}$ ;  $\text{R} = i\text{-Pr, t-Bu, C}_6\text{H}_{11}, \text{Ph}$ )<sup>5</sup> and ketenimines ( $\text{R}_2\text{C}=\text{C}=\text{NR}'$ ;  $\text{R}=\text{Ph}, \text{R}'=\text{CH}_3$ ;  $\text{R}=\text{CH}_3, \text{R}'=\text{Ph}$ ),<sup>6</sup> and that the  $\eta^1\text{-C}$  complex of the isothiocyanate  $\text{CH}_3\text{NCS}$  with  $\text{Na}[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$  is in equilibrium with the metalloheterocycle  $\text{Na}[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})\{\text{C}(\text{S})\text{N}(\text{CH}_3)\text{C}(\text{O})\}]]$ .<sup>7</sup>



Fehlhammer's results suggested that, under some circumstances, the addition of  $\text{CO}_2$  to CO complexes might lead to the formation of isolable metalloanhydride complexes analogous to those which we had proposed as reactive intermediates, and this has led us to further examine the reactivity of  $\text{CO}_2$  and other heteroallenes with electron-rich carbonyl complexes. We were particularly interested in the possibility that metalloheterocycles might be more stable if they were formed by the addition of heteroallenes to a CO complex which, although nucleophilic, was not anionic, and the tungsten complex  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})] \text{ (1)}^8$  was a promising substrate for such reactions since it has been reported to react with methyl iodide to give  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CH}_3)]^+.$ <sup>9</sup> Although we have established that 1 does not form a metalloanhydride with  $\text{CO}_2$ ,

It does form a number of other metalloheterocycles by addition of heteroallenes including isocyanates, isothiocyanates, and carbodiimides, as summarized in Scheme I. We have published a preliminary communication on the formation of the metallocycloimides 2, 3 by addition of isocyanates to 1,<sup>10</sup> and we now wish to report details of those experiments and of the other reactions summarized in Scheme I. These provide the first examples of metalloheterocycle formation by heteroallene addition to a neutral carbonyl complex of a transition metal.

## Experimental Section

**General Data.** All transformations and manipulations involving air-sensitive compounds were performed using either standard Schlenk techniques or a Vacuum Atmospheres drybox under an atmosphere of prepurified nitrogen or argon unless otherwise noted. Glassware was either flame dried under vacuum or dried in an oven (> 4 hr, 120°C) before use. Tetrahydrofuran (THF) and diethyl ether were predried over sodium wire and then distilled from sodium/benzophenone ketyl under nitrogen. Pentane was stirred for two days over concentrated sulfuric acid and then over solid  $K_2CO_3$  for 6 hr before being distilled from  $LiAlH_4$  under nitrogen. Reagent grade acetone (Mallinckrodt) was used as received. The complex  $[W(\eta-C_5H_5)_2(CO)]$  (1) (40% yield) was prepared by a literature procedure,<sup>8b</sup> but in our hands this material was consistently contaminated with 5-10%  $[W(\eta-C_5H_5)_2H_2]$ . Methyl isocyanate (Aldrich), phenyl isocyanate (Aldrich), and phenyl isothiocyanate (Aldrich) were all used as received. Methyl thioisocyanate (Aldrich) was distilled under nitrogen from phosphorous pentasulfide and stored as a THF solution under argon. Carbon dioxide (Matheson) and carbonyl sulfide (Matheson) were also used as received. Diphenylcarbodiimide was prepared by the literature method.<sup>11</sup>

$^1H$  NMR spectra were recorded on a Bruker AM-300 (300 MHz) or a Bruker WM-300-WB (300 MHz) NMR spectrometer. Perdeuteroacetone, -acetonitrile, -dimethylsulfoxide, and -dichloromethane (all 99.5+ atom%) were purchased from Merck, Sharpe, and Dohme or from Cambridge Isotopes and were used as received. Chemical shifts are reported in  $\delta$  using the residual protons of the deuterated solvents as an internal standard.  $^{13}C$  NMR spectra were obtained on a Bruker AM-300 (75.5 MHz) or a Bruker WM-300-WB (75.5 MHz) NMR spectrometer. Chemical shifts are reported in  $\delta$  using the  $^{13}C$  chemical shift of the deuterated solvent

as an internal standard. Infrared spectra were obtained as KBr pellets on a Perkin Elmer 683 grating infrared spectrometer, using the  $1601\text{ cm}^{-1}$  band of polystyrene as an external reference. Mass spectra were recorded on a Kratos MS-9 mass spectrometer. Mass spectral patterns which exhibited the W isotope envelope are reported as the values of m/e which correspond to the species containing the  $^{184}\text{W}$  isotope. Microanalyses were carried out as indicated by Schwarzkopf Microanalytical Laboratory, Woodside, New York (Sch) or by Galbraith Microanalytical Laboratory, Knoxville, Tennessee (Gal). Gas chromatographic analyses were performed on a Perkin Elmer Sigma-300. A thermal conductivity detector and a 3' x 1/8" teflon column packed with 80/100 mesh Poropak Q (Alltech) were used for the analysis of carbon dioxide and carbonyl sulfide.

**X-ray crystallography.** Crystals for X-ray diffraction studies were mounted in glass capillary tubes (Charles Supper Co.) and flame sealed under argon. Data were collected on a Nicolet R3 diffractometer using graphite monochromatized Mo K $\alpha$  radiation (50 kv, 30 ma). Data collection was controlled by the Nicolet P3 program<sup>12</sup> and structures were solved using SHELXTL<sup>13</sup>. Diffractometer data were processed with FOXTAPE, a local modification of the Nicolet program XTAPE. Empirical absorption corrections were performed by the program XEMP (Nicolet) while drawings were generated by the program SNOOPI (part of the Oxford University CHEMGRAF Suite package) or by XPLOT (Nicolet). All molecular calculations were performed with the aid of the program XP (Nicolet). Atomic scattering factors were based on literature values for W<sup>14</sup> and on those in the SHELXTL program for other atoms. Weights were taken as  $[\sigma^2(\text{F}) + g\text{F}^2]^{-1}$ .

$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{CH}_3)\text{C}(\text{O})\}]$  (2). A dark green slurry of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$  (0.65 g, 1.90 mmol) in pentane (60 mL) was treated with 13.0 mL of  $\text{CH}_3\text{NCO}$  (12.6 g, 220.9 mmol) with rapid stirring. Over the course of 2.5 hr, the solution color changed to a bright orange and spectroscopically pure  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{CH}_3)\text{C}(\text{O})\}]$  was deposited as an orange powder. The complex was collected by decantation, washed with pentane (3 x 20 mL), and vacuum dried (0.67 g, 1.68 mmol = 98%). Analytically pure material could be obtained as irregular needles and spars (ca. 90% recovery) by slow cooling to  $-70^\circ\text{C}$  of a saturated acetone solution of the complex. Note: Crystalline samples for analysis were dried under high vacuum for a minimum of 48 hr to remove occluded water. Anal. Calcd for  $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{W}$ : C, 39.12; H, 3.29; N, 3.51. Found (Sch): C, 39.06; H, 3.37; N, 3.58.  $^1\text{H}$  NMR (300 MHz, acetonitrile- $d_3$ ):  $\delta$  4.91 (s, 10H,  $2\text{C}_5\text{H}_5$ ), 2.34 (s, 3H,  $\text{NCH}_3$ ).  $^{13}\text{C}$  NMR (75.5 MHz, gated decoupled, dimethylsulfoxide- $d_6$ ):  $\delta$  176.2 (s, 2C, satellites  $J_{183\text{W-C}} = 93.4$  Hz,  $2\{\text{W-C}(\text{O})\}$ ), 83.6 (d, 10C,  $^1J_{\text{C-H}} = 183.2$  Hz,  $2\text{C}_5\text{H}_5$ ), 22.8 (q, 1C,  $^1J_{\text{C-H}} = 137.7$  Hz,  $\text{CH}_3$ ). IR (KBr): 3100 ms, 2930 w br, 2865 w, 1721 m, 1679 ms, 1663 ms, 1605 s br, 1411 ms, 1391 ms, 1364 w, 1304 s br, 1254 ms, 1103 mw, 1065 w br, 1011 m, 995 m, 948 ms br, 896 ms, 839 ms, 792 m, 770 m, 609 ms, 601 ms, 485 mw br, 419 m, 378 m  $\text{cm}^{-1}$ . Mass spectrum (parent ion,  $^{184}\text{W}$ ) m/e 399.

$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{O})\}]$  (3). A dark green slurry of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$  (0.25 g, 0.73 mmol) in pentane (25 mL) was treated with 3.0 mL of  $\text{PhNCO}$  (3.27 g, 27.4 mmol) with stirring. Reaction was instantaneous, as evidenced by a rapid solution color change to orange and the immediate deposition of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{O})\}]$  as a pale orange powder. After 1 hr, the complex was collected by decantation, washed with pentane (3 x 20 mL), and dried in vacuo (0.32 g, 0.69 mmol = 95%). Anal. Calcd for  $\text{C}_{18}\text{H}_{15}\text{NO}_2\text{W}$ : C, 46.87; H, 3.28; N, 3.04.



Found (Gal): C, 47.10; H, 3.30; N, 3.15.  $^1\text{H}$  NMR (300 MHz, acetone- $\text{d}_6$ ):  $\delta$  7.40–7.05 (c, 5H,  $\text{C}_6\text{H}_5$ ), 5.11 (s, 10H,  $2\text{C}_5\text{H}_5$ ).  $^{13}\text{C}$  NMR (75.5 MHz, broad band decoupled,  $0^\circ\text{C}$ , dichloromethane- $\text{d}_2$ ):  $\delta$  176.6 (s, 2C, satellites  $J_{183\text{W}-\text{C}} = 91.6$  Hz,  $2\{\text{W}-\text{C}(\text{O})\}$ ), 134.5 (s, 1C,  $\text{C}_6\text{H}_5$ -ipso), 128.7, 123.7 (both s, 4C, ( $\text{C}_6\text{H}_5$ -ortho, meta), 126.0 (s, 1C,  $\text{C}_6\text{H}_5$ -para), 84.4 (s, 10C,  $2\text{C}_5\text{H}_5$ ). IR (KBr): 3100 m, 3065 m, 1709 ms, 1625 s br, 1594 ms sh, 1579 m, 1545 mw, 1489 m br, 1452 m, 1428 mw, 1412 mw, 1384 mw, 1292 s br, 1178 mw, 1110 ms, 1091 ms, 1048 m, 1012 w, 990 w, 909 mw, 841 m, 778 m, 745 ms, 696 ms, 628 m, 610 m, 601 m, 558 m, 499 m, 390 mw br  $\text{cm}^{-1}$ .

$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$  (4). To a dark green solution of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2-(\text{CO})]$  (0.29 g, 0.85 mmol) in diethyl ether (25 mL) was added 3.0 mL of diphenylcarbodiimide (3 g, 15 mmol) with stirring. Over a 2 hr period, the solution color changed to orange and spectroscopically pure  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$  was deposited as a yellow powder. The solid was collected by decantation, washed with diethyl ether (3 x 20 mL), and dried in vacuo (0.43 g, 0.80 mmol = 94%). Analytically pure material could be obtained as yellow flakes (ca. 35% recovery) via slow cooling to  $-70^\circ\text{C}$  of a saturated acetone solution of the complex. Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{OW}$ : C, 53.75; H, 3.77; N, 5.22. Found (Gal): C, 53.75; H, 3.63; N, 5.38.  $^1\text{H}$  NMR (300 MHz, dimethylsulfoxide- $\text{d}_6$ ):  $\delta$  7.46–6.77 (c, 10H,  $2\text{C}_6\text{H}_5$ ), 4.98 (s, 10H,  $2\text{C}_5\text{H}_5$ ).  $^{13}\text{C}$  NMR (75.5 MHz, broad band decoupled,  $0^\circ\text{C}$ , dichloromethane- $\text{d}_2$ ):  $\delta$  172.7 (s, 1C,  $\text{W}-\text{C}(\text{O})$ ), 154.5, 154.3, 135.6 (all s, 3C,  $2(\text{C}_6\text{H}_5\text{-ipso}) + \text{W}-\text{C}(\text{NPh})$ ), 128.6, 128.4, 125.3, 121.0 (all s, 8C,  $2(\text{C}_6\text{H}_5\text{-ortho, meta})$ ), 125.9, 121.9 (both s, 2C,  $2(\text{C}_6\text{H}_5\text{-para})$ ), 84.1 (s, 10C,  $2\text{C}_5\text{H}_5$ ). IR (KBr): 3132 mw, 3114 mw, 3089 m, 3060 mw, 3031 mw, 1674 s, 1595 vs br, 1487 s, 1453 m, 1448 m, 1412 ms, 1386 mw, 1364 ms, 1321 ms sh, 1305 s br, 1250 ms, 1174 mw, 1161 m, 1153 m, 1131 s, 1101 s, 1071 ms, 1026 mw, 1014 m, 990

ms, 942 w, 921 mw, 899 ms, 882 m, 861 ms, 839 ms, 816 m, 780 s, 761 s, 739 s, 704 s, 698 s, 625 mw, 603 ms, 592 ms, 583 ms, 548 mw, 535 ms, 500 ms, 478 w, 430 m, 403 mw sh, 389 m, 337 m sh, 327 m  $\text{cm}^{-1}$ .

$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$  (5). A dark green solution of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$  (0.27 g, 0.79 mmol) in diethyl ether (20 mL) was treated with 2.5 mL of PhNCS (2.82 g, 20.9 mmol) with stirring. Reaction was immediate as evidenced by a solution color change to orange and the deposition of spectroscopically pure  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$  as a dark orange powder. After 4 hr the complex was collected by decantation, washed with diethyl ether (4 x 20 mL), and dried in vacuo (0.37 g, 0.67 mmol = 85%). Analytically pure material could be obtained as small orange-red flakes (ca. 30% recovery) via slow cooling to  $-70^\circ\text{C}$  of a saturated acetone solution of the complex. Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{SW}$ : C, 52.18; H, 3.66. Found (Sch): C, 52.19; H, 3.74.  $^1\text{H}$  NMR (300 MHz, dimethylsulfoxide- $\text{d}_6$ ):  $\delta$  7.40–6.80 (C, 10H,  $2\text{C}_6\text{H}_5$ ), 5.02 (s, 10H,  $2\text{C}_5\text{H}_5$ ).  $^{13}\text{C}$  NMR (75.5 MHz, broad band decoupled,  $0^\circ\text{C}$ , dichloromethane- $\text{d}_2$ ):  $\delta$  221.2 (s, 1C, W-C(S)), 153.3, 150.3, 138.6 (all s, 3C,  $2(\text{C}_6\text{H}_5\text{-ipso}) + \text{W-C}(\text{NPh})$ ), 128.7, 127.1, 120.6 (all s, 8C,  $2(\text{C}_6\text{H}_5\text{-ortho, meta})$ ), 127.5, 122.4 (both s, 2C,  $2(\text{C}_6\text{H}_5\text{-para})$ ), 86.4 (s, 10C,  $2\text{C}_5\text{H}_5$ ). IR (KBr): 3080 m, 3045 mw, 1612 s, 1587 s, 1453 ms, 1448 w, 1443 mw, 1409 m, 1390 mw, 1356 mw, 1325 s, 1308 m sh, 1244 m sh, 1236 m, 1199 s, 1168 m sh, 1100 ms, 1085 m sh, 1063 m, 1028 mw, 1011 mw, 988 m, 943 mw, 922 w, 909 w, 899 mw, 890 m, 879 m, 860 m, 847 mw, 834 m, 812 w, 774 m, 763 m, 750 m, 704 s, 599 w, 574 m, 549 ms, 520 m, 496 w, 465 w, 416 w, 400 w, 382 m  $\text{cm}^{-1}$ .

$[W(\eta-C_5H_5)_2\{C(O)N(CH_3)C(S)\}]$  (8). A 3.06 M solution of  $CH_3NCS$  in THF (12.0 mL = 36.7 mmol) was added to a dark green solution of  $[W(\eta-C_5H_5)_2(CO)]$  (0.71 g, 2.08 mmol) in diethyl ether (20 mL) with stirring. After 17 hr, the solution color had changed to a cherry-red and spectroscopically pure  $[W(\eta-C_5H_5)_2\{C(O)N(CH_3)C(S)\}]$  had been deposited as a rust-orange powder. The complex was collected by decantation, washed with diethyl ether (2 x 10 mL), and dried in vacuo (0.59 g, 1.42 mmol = 68%). Analytically pure material could be obtained as small orange-red flakes (ca. 60% recovery) via slow cooling to  $-70^\circ C$  of a saturated diethyl ether/tetrahydrofuran solution (v/v 13:1) of the complex. Anal. Calcd for  $C_{13}H_{13}NOSW$ : C, 37.61; H, 3.16; N, 3.37. Found (Gal): C, 37.76; H, 3.38; N, 3.35.  $^1H$  NMR (300 MHz, acetone- $d_6$ ):  $\delta$  5.01 (s, 10H,  $2C_5H_5$ ), 2.71 (s, 3H,  $NCH_3$ ).  $^{13}C$  NMR (75.5 MHz, gated decoupled,  $0^\circ C$ , dichloromethane- $d_2$ ):  $\delta$  228.9 (s, 1C,  $W-C(S)$ ), 171.1 (s, 1C,  $W-C(O)$ ), 86.0 (d, 10C,  $^1J_{C-H} = 183.2$  Hz,  $2C_5H_5$ ), 28.9 (q, 1C,  $^1J_{C-H} = 139.9$  Hz,  $NCH_3$ ). IR (KBr): 3120 mw, 3085 m, 2925 mw, 1800 mw, 1734 m, 1672 s br, 1643 s sh, 1448 mw, 1435 mw, 1410 s, 1398 s, 1372 m, 1332 s, 1235 s br, 1070 s br, 1012 m, 980 m, 930 s, 891 m, 868 ms, 836 ms, 804 m, 718 ms, 607 ms, 596 m, 582 ms, 512 w, 478 ms, 410 s, 386 ms, 354 m  $cm^{-1}$ . Mass spectrum (parent ion  $^{184}W$ ) m/e 415.

**X-ray Diffraction Study of  $[W(\eta-C_5H_5)_2\{C(S)N(Ph)C(NPh)\}]$ .** Bright orange parallelepipeds of  $[W(\eta-C_5H_5)_2\{C(S)N(Ph)C(NPh)\}]$  were grown by slow vapor diffusion (days) of diethyl ether into a saturated acetone solution of the complex. A crystal of dimensions 0.1 x 0.2 x 0.2 mm mounted in a 0.2 mm capillary tube was used for the diffraction study. The unit cell was indexed using 15 reflections from the rotation photograph. Two angles were near  $90^\circ$ , and a lattice determination using both the P3 program<sup>12</sup> and TRACER<sup>15</sup> yielded a monoclinic cell. Examination of axial photographs confirmed this assignment since only the

b-axis possessed mirror symmetry. A trial data collection revealed systematic absences which uniquely determined the space group as  $P 2_1/n$  (nonstandard setting of  $P 2_1/c$ ). The final unit cell parameters were obtained by a least squares refinement of the angles obtained from 12 selected Friedel pairs in the range  $20^\circ \leq 2\theta \leq 30^\circ$ , and a single quadrant of data  $\{(hkl): +h, +k, \pm l\}$  was collected. Full details of the data collection are presented in Table I. The intensities of three check reflections measured after every 60 reflections indicated no significant crystal decay after 73 hr of exposure. A semi-empirical absorption correction based on  $\psi$  scans from 9 reflections in the range  $6^\circ \leq 2\theta \leq 40^\circ$  and Lorentz and polarization corrections were applied to the data.

A sharpened Patterson map readily revealed the position of the W atom, and a difference map, calculated after refining the scale factor, the isotropic temperature factor, and the positional parameters of the W atom ( $R = 18\%$ ), revealed the positions of the 2 nitrogen atoms, the sulfur atom, and 11 of the 24 carbon atoms. Least squares refinement ( $R = 12\%$ ) revealed the remaining 13 carbon atoms. At this point, hydrogen atoms were placed in calculated positions on the appropriate carbon atoms ( $U_{iso}(H) = 1.2 \times U_{iso}(C)$ ;  $d_{C-H} = 0.96 \text{ \AA}$ ) and all non-hydrogen atoms were made anisotropic. Refinement was then performed to convergence ( $\Delta/\sigma(\max) \leq 0.1$ ) using the blocked-cascade least squares procedure of SHELXTL. The value of the  $F^2$  multiplier was adjusted so that a normal probability plot<sup>16</sup> gave a slope as close to 1.0 as possible. The largest peak in the final difference map had a density of  $1.16 \text{ e}^-/\text{\AA}^3$  and was located near one of the cyclopentadienyl rings; all others had densities  $< 0.88 \text{ e}^-/\text{\AA}^3$ . Final atomic positional parameters for non-hydrogen atoms are presented in Table II. Anisotropic thermal parameters, and calculated hydrogen parameters, least square planes and interplanar angles and angles about tungsten are given in Tables SI, SII, and SIII of the Supplementary Material.

## Results and Discussion

### Metallocycloimide Formation by Isocyanate Addition to $[W(\eta-C_5H_5)_2(CO)]$

(1). The feasibility of heteroallene addition to 1 was initially established by the reaction of a large excess of  $CH_3NCO$  with a dark green slurry of 1 in pentane at room temperature. This resulted in precipitation of a bright orange powder which was shown by  $^1H$  NMR to be a spectroscopically pure sample of a methyl isocyanate adduct of 1. The most reasonable formulation of this adduct was as the metallocycloimide  $[W(\eta-C_5H_5)_2\{C(O)N(CH_3)C(O)\}]$  (2) shown in Scheme I, and this was confirmed by a single crystal x-ray diffraction study of an orange-yellow cube grown by cooling a saturated acetone solution to  $0^\circ C$  over a 4 hr period. Details of the diffraction study will not be repeated since they are available in our previous communication and in the Supplementary Material to that communication, but the study established the molecular geometry for 2 shown in Fig. 1 and the dimensions listed in Tables III and IV.

The diffraction study established that 2 can be described as a metallocycloimide with a metallocyclic core reminiscent of the structure of a typical organic cyclic imide.<sup>17</sup> The metal atom, the ring carbons and the nitrogen atom are essentially coplanar, with the maximum deviation of any one atom from the mean ring plane being 0.023 Å. The planar arrangement about nitrogen (the methyl carbon is only 0.017 Å off the metallocycle plane) would suggest that the nitrogen lone pair is delocalized into the metallocycloimide framework, and, consistent with this, the nitrogen to acyl carbon bond lengths of 1.393 (4) Å are significantly shortened relative to a typical C-N single bond length of ca. 1.47 Å<sup>18</sup>. The 4-membered ring might be expected to result in a significant strain energy within the molecule, but although the N(1)-C(1)-W bond angle of  $97.4 (2)^\circ$  does indicate distortion of the trigonal angles about the acyl carbon, much of the compression enforced by the ring size is taken up by the C(1)-W-C(1')

angle which, at 60.3 (2)° is significantly smaller than the CWC angles of 75.4° in  $[W(\eta-C_5H_5)_2\{CH_2C_6H_3(CH_3)_2\}_2]^{19}$  and 75.6° in  $[W(\eta-C_5H_5)_2(CH_2CH_2PMe_2Ph)CH_3]^+$ ,<sup>20</sup> the only other crystallographically characterized d<sup>2</sup> tungstenocene complexes with W-C  $\sigma$  bonds. The rather large value of 139.4 (3)° for the W-C(1)-O(1) angle probably reflects nonbonding interactions between the acyl oxygens and the non-bonding pair of electrons on the metal center, which would be expected to occupy the Alcock orbital,<sup>21</sup> normal to the plane that bisects the C(1)-W-C(1') angle. It is well established that electrons in this orbital are stereochemically active in d<sup>1</sup> and d<sup>2</sup> bent metallocene complexes.<sup>22</sup>

Formation of metallocycloimides from 1 is not limited to methylisocyanate, and a dark green slurry of 1 in pentane reacted readily with excess PhNCO at room temperature to deposit a dull orange powder which was readily established by <sup>1</sup>H NMR to have the composition expected for an adduct of 1 with PhNCO. Formulation of this as  $[W(\eta-C_5H_5)_2\{C(O)N(Ph)C(O)\}]$  (3) was strongly supported by comparison of the gated-decoupled <sup>13</sup>C NMR spectrum of 3 with that of 2 (Table V). Both spectra contained singlets with satellites attributable to single bond coupling to <sup>183</sup>W (14% abundance, I = ½) at  $\delta$  176.2 and 176.6, respectively, which could be assigned to the acyl carbons bonded to W. The chemical shifts of these resonances are somewhat low for acyl carbons bonded to tungsten (typically above  $\delta$  200<sup>23</sup>), but a unique chemical shift is not unreasonable given the distortions enforced on the trigonal carbon by participation in a four membered metallocycle and the delocalization of the nitrogen lone pair into the metallocycloimide ring.

As summarized in Scheme II there are two reasonable mechanisms for the formation of metallocycloimides 2 and 3 from 1. The simplest mechanism would involve direct 2+2 cycloaddition of the isocyanate to the metal carbonyl bond, but it is also possible that the reaction involves initial  $\eta^1$ -C coordination of

the isocyanates to the basic metal center. In the zwitterionic intermediate, the heteroallene is nucleophilic at the  $\beta$ -position and the carbonyl is electrophilic at the  $\alpha$ -position, and subsequent ring closure would give the 4-membered metalloheterocycle. Although we have no direct experimental evidence which would discriminate between these mechanisms, we feel that an  $\eta^1$ -C complex is likely to be at least a transient intermediate, primarily because of the analogy with the addition of heteroallenes to  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]^-$ .<sup>3,5,6,7</sup> In the case of  $\text{CH}_3\text{N}=\text{C}=\text{S}$  Fehlhhammer has established, for example, that the  $\eta^1$ -C complex is in equilibrium with the metalloheterocycle,<sup>7</sup> and we have reported labelling studies which suggest that the same is true for the complex of  $\text{CO}_2$  with  $\text{Na}[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ .<sup>3</sup> Ring closure through nitrogen probably reflects the greater strength of C=O bonds as compared with C=N bonds: the isomeric metallocycloisoimides contain 1C=O and 1C=N bond in place of the 2C=O bonds in 2 and 3.<sup>24</sup>

There are no previous reports of the formation of metallocycloimide complexes, but it seems probable that metallocycloisoimides are intermediates in the previously reported<sup>25</sup> formation of isocyanide complexes by reaction of isocyanates with carbonyls of the group 6 and 8 metals (Scheme III).

**Metallocycloacylamidine Formation by Carbodiimide Addition to  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ .** Diphenylcarbodiimide, like isocyanates, added readily to the W-CO group in 1, and after 2 hr in diethyl ether at room temperature the dark green color of 1 was essentially discharged to leave an orange solution and a yellow solid precipitate. The solid was collected by decantation, washed with diethyl ether and vacuum dried to give spectroscopically pure samples of material indicated by  $^1\text{H}$  NMR to be a simple adduct of 1 and  $\text{PhN}=\text{C}=\text{NPh}$ . Analytically pure material could be obtained by recrystallization from acetone

at low temperature and was formulated as the metallocycloacylamidine  $[W(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$  (4) (Scheme I) primarily on the basis of  $^{13}\text{C}$  NMR data which established the presence of two ( $\eta^5\text{-C}_5\text{H}_5$ ) ligands and two inequivalent phenyl groups. The  $^{13}\text{C}$  NMR spectrum also contained resonances indicating the presence of two carbons which did not carry hydrogens, one of which was at a position indicative of an acyl group  $\alpha$  to W (Table IV) and the second of which at  $\delta$  154.5 could reasonably be assigned to the amidine carbon  $\alpha$  to W.

Fehlhammer has previously reported the formation of a metallocycloacylamidines by addition of diimides to  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]^-$ ,<sup>5</sup> and, as in that case, we propose that the formation of 4 most probably involves formation of an intermediate  $\eta^1\text{-C}$  carbodiimide complex as shown in Scheme IV.

**Metallocyclothioacylamidine Formation by Phenylisothiocyanate Addition to  $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ .** The most surprising metalloheterocycle formed by heteroallene addition to 1 was that obtained when  $\text{S}=\text{C}=\text{NPh}$  was added to 1 in diethyl ether at room temperature. This resulted in immediate discharge of the dark green color of 1 to give an orange solution and a dark orange precipitate which  $^1\text{H}$  NMR established as a tungstenocene derivative which contained two inequivalent phenyl rings, indicative of the incorporation of fragments of two isothiocyanate molecules into the product.

The single crystal x-ray diffraction study described in the Experimental Section established that this was the metallocyclothioacylamidine  $[W(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$  (5). The structure of the molecule is illustrated in Figure 2, and bond lengths and angles within the molecule are presented in Tables VI and VII.

Complex 5 contains a 4-membered metallocyclic ring defined by W, C(1), C(2), and N(1), and, like the metallocyclic ring in the metallocycloimide 2, this is essentially planar with the maximum deviation of any one atom from the



plane being 0.004 Å. The ring nitrogen N(1) is almost planar and lies 0.031 Å off the plane defined by C(1), C(2), and the ipso carbon C(41). This is consistent with delocalization of the nitrogen lone pair into the metallocyclic framework as indicated by the short N-C single bond distances of 1.393(12) Å and at 1.416(13) Å for the C(1)-N(1) and C(2)-N(1) bonds. These values are intermediate between the values of 1.43 Å for typical  $sp^2$  C-N bonds and 1.333 Å in N-C=O groups.<sup>18</sup>

The dimensions of the metallocyclothioacylamidine group in **5** are similar to those of the metallocycles in the cobalt complexes  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)\{\text{C}(\text{S})\text{N}(\text{Me})\text{-N}(\text{R})\}]$  ( $\text{R}=\text{CH}_3$ , Ph),<sup>26</sup> which provide the only previously reported examples of this functional group. It is particularly interesting to note that the C(1)-W-C(2) angle of  $61.9(4)^\circ$  (which is equal, within experimental error, to the analogous angle in **2**) is similar to the C-M-C angles in the cobalt complexes, indicating that the acute value (see discussion of **2** above) is intrinsic to this functional group and is not a function of the sterically crowded environment in the tungstenocene systems. The only significant differences between the overall geometry of **5** and that of the cobalt complexes are the large values of  $139.4(6)^\circ$  and  $144.9(7)^\circ$  for the W-C(1)-S(1) and W-C(2)-N(2) angles. These are significantly larger than the similar Co angles, and probably (as in the case of **2**) reflect non-bonding interactions between the functionalities exo to the ring and the non-bonding electrons on the tungsten center located in the Alcock orbital (see above).

The surprising formation of **5** can be accounted for in terms of the mechanism in Scheme V, in which transient  $\eta^1\text{-C}$  coordination of the isothiocyanate leads to metallocycle **6** which can generate an intermediate isonitrile complex **7** by elimination of COS. Addition of a second equivalent of isothiocyanate to **7**, probably again via an intermediate  $\eta^1\text{-C}$  heteroallene

complex, could lead to the observed metallocyclothioacylamidine 5. There is no direct precedent for the formation of an isonitrile complex like 7 in this system, but 7 would be isoelectronic with 1 and is a reasonable potential intermediate. This mechanism is strongly supported by a GC study which indicated the generation of 1.1 ( $\pm$  0.2) moles of COS for each mole of 1. The intermediacy of 7 in the formation of 5 would also be consistent with Werner's previous syntheses of the cobalt complexes  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)\{\text{C}(\text{S})\text{N}(\text{Me})\text{N}(\text{R})\}](\text{R} = \text{CH}_3, \text{Ph})$ , by addition of isothiocyanates to the isonitrile complex  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{CNCH}_3)]$ .<sup>26</sup>

**Metallocycloacylthioamide Formation by Isothiocyanate Addition to 1.** A surprising feature of the mechanism in Scheme V is that the first  $\eta^1\text{-C}$  isothiocyanate complex ring closes through sulfur to give 6 while the second ring closes through nitrogen to give 5. This implies that metallocycle formation is either readily reversible, so that the outcome of the reaction is thermodynamically controlled by loss of gaseous COS, or that there is a fine kinetic balance in  $\eta^1\text{-C}$  isothiocyanate complexes between ring closure through sulfur and ring closure through nitrogen. We cannot rule out the possibility that these reactions are reversible, but comparison of the reaction of  $\text{S}=\text{C}=\text{NCH}_3$  with 1 with the reaction of  $\text{S}=\text{C}=\text{NPh}$  with 1 suggests that there is indeed a fine balance between these competing modes of ring closure.

The reaction of  $\text{S}=\text{C}=\text{NCH}_3$  with 1 was initially carried out by adding excess  $\text{S}=\text{C}=\text{NCH}_3$  in THF to a dark green solution of 1 in diethyl ether at room temperature. This resulted in a slow color change to a cherry red solution, with concurrent deposition of a rust orange powder which could be recrystallized from THF/diethyl ether at low temperatures as red orange flakes. Analysis and  $^1\text{H}$  NMR established that these crystals were those of a monoisothiocyanate adduct of 1, and comparison of the  $^{13}\text{C}$  NMR spectrum of the complex with those of

the previously characterized metalloheterocycles within this system (Table V) unambiguously established that the molecule contained an acyl group and a thioacyl group, and that the adduct was therefore the metallocycloacylthioamide  $[W(\eta-C_5H_5)_2\{C(S)N(CH_3)C(O)\}]$  (8). This could be formed as shown in Scheme VI by ring closure through nitrogen within an intermediate  $\eta^1-C$  isothiocyanate complex.

The switch from a preference for initial ring closure through sulfur and ultimate formation of 5 in the  $S=C=NPh$  reaction, to initial ring closure through nitrogen and formation of 8 in the  $S=C=NMe$  reaction, can be rationalized in terms of an increase in the nucleophilicity of the nitrogen because of the methyl substituent. The ring closure mode is, however, finely balanced, and the ether supernatant contained small quantities of a second product which became a major product when the  $S=C=NCH_3$  reaction was carried out in pentane instead of diethyl ether. Under these conditions the reaction yielded a mixture of two products - 8 (53%) and a second metalloheterocycle (27%) with a  $^1H$  NMR spectrum containing a singlet cyclopentadienyl resonance at  $\delta$  4.98 and methyl resonances at  $\delta$  3.00 and 2.97. This suggested that the second material contained fragments derived from two isothiocyanate molecules, and examination of the  $^{13}C$  NMR spectrum of the material in  $CD_2Cl_2$  has led us to formulate the compound as  $[W(\eta-C_5H_5)_2\{C(NCH_3)N(CH_3)C(S)\}]$  (9) on the basis of the observation of resonance attributable to N-iminoacyl and a thioacyl group (Table V). We have been unable to separate 9 from 8 and, hence, unable to definitely characterize 9, but the similarity to 6 leaves little doubt that 9 is the double addition product, presumably formed by a mechanism similar to that in Scheme V.

Addition of Other Heteroallenes to 1. As previously reported<sup>10</sup> we have been unable to form a metalloanhydride by addition of CO<sub>2</sub> to 1, but most other heteroallenes react with 1. In addition to those discussed above we have, for example, observed that 1 will react with CS<sub>2</sub>, COS, S=C=NtBu and O=C=CPh<sub>2</sub>. None of these reactions gave tractable organometallic products, however, and they have not, therefore, been examined in detail.

### Conclusion

It is clear from the results above that metalloheterocycle formation by addition of heteroallenes to carbonyl complexes is not limited to anionic carbonyl complexes, but that electron-rich neutral carbonyls can also participate in such reactions. In the specific case of [W( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)], heteroallene addition provides access to a number of novel metalloheterocycles of which the metallocycloimides 2 and 3 and the metallocycloacylthioamide 8 provide the first reported examples of these particular functional groups. These complexes will probably have a significant reaction chemistry and efforts to develop this chemistry with the objective of discovering new approaches to the incorporation of heteroallene derived fragments in organic molecules are currently underway in our group.

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**Supplementary Material Available:** Tables of anisotropic temperature factors, calculated hydrogen parameters, least squares planes, interplanar angles and angles about tungsten in 5 (3 pages); structure factor tables for 5 (15 pages); figure of packing within unit cell for 5 (1 page). Ordering information is given on any current masthead page.

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Figure 1. Molecular structure of  $[W(\eta-C_5H_5)_2\{C(O)N(CH_3)C(O)\}]$  (50% probability ellipsoids). Atoms with an A suffix are symmetry generated by the plane through the W and N atoms perpendicular to the metallocycloimide plane.

Figure 2. Molecular structure of  $[W(\eta-C_5H_5)_2\{C(S)N(Ph)C(NPh)\}]$  (50% probability ellipsoids).



Scheme I. Products of Heteroallene Addition to  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ .

Scheme II. Possible Mechanisms for Metallocycloimide Formation from 1.

Scheme III. Probable Mechanism for the Formation of an Isocyanide Ligand by Addition of an Isocyanate to  $[\text{Mo}(\text{CO})_6]$ .

Scheme IV. Proposed Mechanism for the Formation of 4.

Scheme V. Proposed Mechanism for the Formation of 5.

Scheme VI. Proposed Mechanism for the Formation of 8.

Table I. Summary of Crystallographic Data for  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$

### Crystal Data

Space group	P 21/n
a (Å)	7.816 (2)
b (Å)	19.838 (5)
c (Å)	13.066 (3)
$\beta$ (deg)	92.33 (2)
V (Å <sup>3</sup> )	2024.4 (9)
Z	4
$\mu$ (cm <sup>-1</sup> )	61.39
$d_c$ (g/mL)	1.81
$d_o$ (g/mL)	--
T (°C)	25
$\lambda$ (Å)	0.71069

### Data Collection

Scan type	2 $\theta$ : $\theta$
Max 2 $\theta$ (deg)	50
Min 2 $\theta$ (deg)	3
Scan range (deg)	1.8 (symmetrical)
Scan speed (deg/min)	3.5 - 19.5
Background/scan ratio	0.5
Total reflections	4227
Unique reflections ( $I > 3\sigma(I)$ , $F > 3\sigma(F)$ )	2469

### Agreement Factors

Final R (%) <sup>a</sup>	4.70
Final $R_w$ (%) <sup>b</sup>	3.77
Goodness of fit (GOF) <sup>c</sup>	1.118
$\sigma$ value	0.00031

$$R = \frac{\sum |F_{\text{obs}} - F_{\text{calc}}|}{\sum |F_{\text{obs}}|}$$

$$R_w = \frac{\sum (w)^{1/2} (F_{\text{obs}} - F_{\text{calc}})}{\sum (w)^{1/2} F_{\text{obs}}}$$

$$\text{GOF} = [\sum w (|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

Table II. Atomic Coordinates<sup>a</sup> for the Non-Hydrogen Atoms of  
 $[W(\eta-C_5H_5)_2\{C(S)N(Ph)C(NPh)\}]$ .

Atom <sup>b</sup>	X/A	Y/B	Z/C
W	8004.5 (5)	8169.2 (2)	-190.4 (3)
C(1)	7251 (14)	9085 (6)	655 (8)
C(2)	6594 (12)	8038 (5)	1205 (7)
C(11)	7373 (16)	7790 (6)	-1778 (9)
C(12)	6214 (14)	7479 (7)	-1116 (8)
C(13)	5166 (14)	7993 (7)	-728 (9)
C(14)	5636 (16)	8608 (7)	-1157 (9)
C(15)	7013 (15)	8480 (7)	-1780 (9)
C(21)	10569 (13)	7769 (6)	-622 (8)
C(22)	10792 (13)	8481 (6)	-436 (10)
C(23)	10534 (14)	8599 (7)	602 (9)
C(24)	10135 (15)	7983 (7)	1060 (9)
C(25)	10127 (14)	7471 (7)	320 (9)
C(31)	6018 (13)	6929 (5)	1547 (7)
C(32)	4686 (15)	6589 (6)	1036 (9)
C(33)	4691 (18)	5907 (6)	887 (10)
C(34)	6030 (19)	5524 (7)	1263 (10)
C(35)	7398 (20)	5835 (6)	1762 (10)
C(36)	7387 (16)	6530 (6)	1921 (9)
C(41)	5546 (13)	9021 (5)	2262 (8)
C(42)	4017 (14)	9344 (6)	2039 (9)
C(43)	3074 (18)	9579 (8)	2849 (12)
C(44)	3667 (20)	9500 (8)	3847 (12)
C(45)	5148 (23)	9165 (6)	4049 (10)
C(46)	6101 (17)	8924 (5)	3247 (9)
N(1)	6457 (11)	8735 (4)	1427 (6)
N(2)	5899 (11)	7607 (4)	1791 (6)
S(1)	7392 (4)	9893 (2)	567 (3)

<sup>a</sup>Fractional atomic coordinates ( $\times 10^4$ ).

<sup>b</sup>See Figure 1 for atom designations.

Table III. Bond Lengths (Å) within  $[W(\eta-C_5H_5)_2\{C(O)N(CH_3)C(O)\}].^a$

---

W-C(1)	2.195 (3)	C(11)-C(12)	1.431 (5)	C(1)-O(1)	1.213 (5)
W-C(11)	2.234 (6)	C(12)-C(13)	1.429 (5)	C(1)-N(1)	1.393 (4)
W-C(12)	2.275 (4)	C(13)-C(13A)	1.403 (8)	N(1)-C(2)	1.451 (7)
W-C(13)	2.351 (3)	C(21)-C(22)	1.433 (6)		
W-C(21)	2.241 (5)	C(22)-C(23)	1.420 (6)		
W-C(22)	2.275 (4)	C(23)-C(23A)	1.387 (11)		
W-C(23)	2.343 (4)				

---

<sup>a</sup>See Figure 1 for atom designations.

Table IV. Bond Angles (deg) within  $[W(\eta-C_5H_5)_2\{C(O)N(CH_3)C(O)\}].^a$

---

C(11)-C(12)-C(13)	106.9 (4)	W-C(1)-O(1)	139.4 (3)
C(12)-C(13)-C(13A)	108.8 (2)	W-C(1)-N(1)	97.4 (2)
C(12)-C(11)-C(12A)	108.6 (5)	N(1)-C(1)-O(1)	123.1 (3)
C(21)-C(22)-C(23)	106.5 (4)	C(1)-N(1)-C(2)	127.5 (2)
C(22)-C(23)-C(23A)	109.3 (3)	C(1)-W-C(1A)	60.3 (2)
C(22)-C(21)-C(22A)	108.4 (5)	C(1)-N(1)-C(1A)	104.7 (4)

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<sup>a</sup>See Figure 1 for atom designations.

Table V.  $^{13}\text{C}$  Resonances of Ring Carbons in Metalloheterocycles  
of the Type  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{X})\text{Y}\text{C}(\text{Z})\}]^{\text{a}}$

Complex	$\delta$ acyl	$\delta$ iminoacyl	$\delta$ thioacyl
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{CH}_3)\text{C}(\text{O})\}]$ 2	176.2		
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{O})\}]$ 3	176.6		
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$ 4	172.7	154.5 or 154.3 <sup>b</sup>	
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$ 5		153.3 or 150.3 <sup>b</sup>	221.1
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{CH}_3)\text{C}(\text{O})\}]$ 8	171.1		228.9
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{CH}_3)\text{C}(\text{NCH}_3)\}]$ 9		150.3	216.2

<sup>a</sup>See Experimental Section for full  $^{13}\text{C}$  spectra of these molecules

<sup>b</sup>The ipso carbons of the iminophenyls in 4 and 5 have chemical shifts similar to those of the iminoacyl carbons and it was not possible to make definitive assignments. The solubilities of the complexes were inadequate for the observation of  $^1\text{J}_{\text{W-C}}$  coupling to the iminoacyl carbons.

Table VI. Bond Lengths (Å) within  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]\text{.}^{\text{a}}$

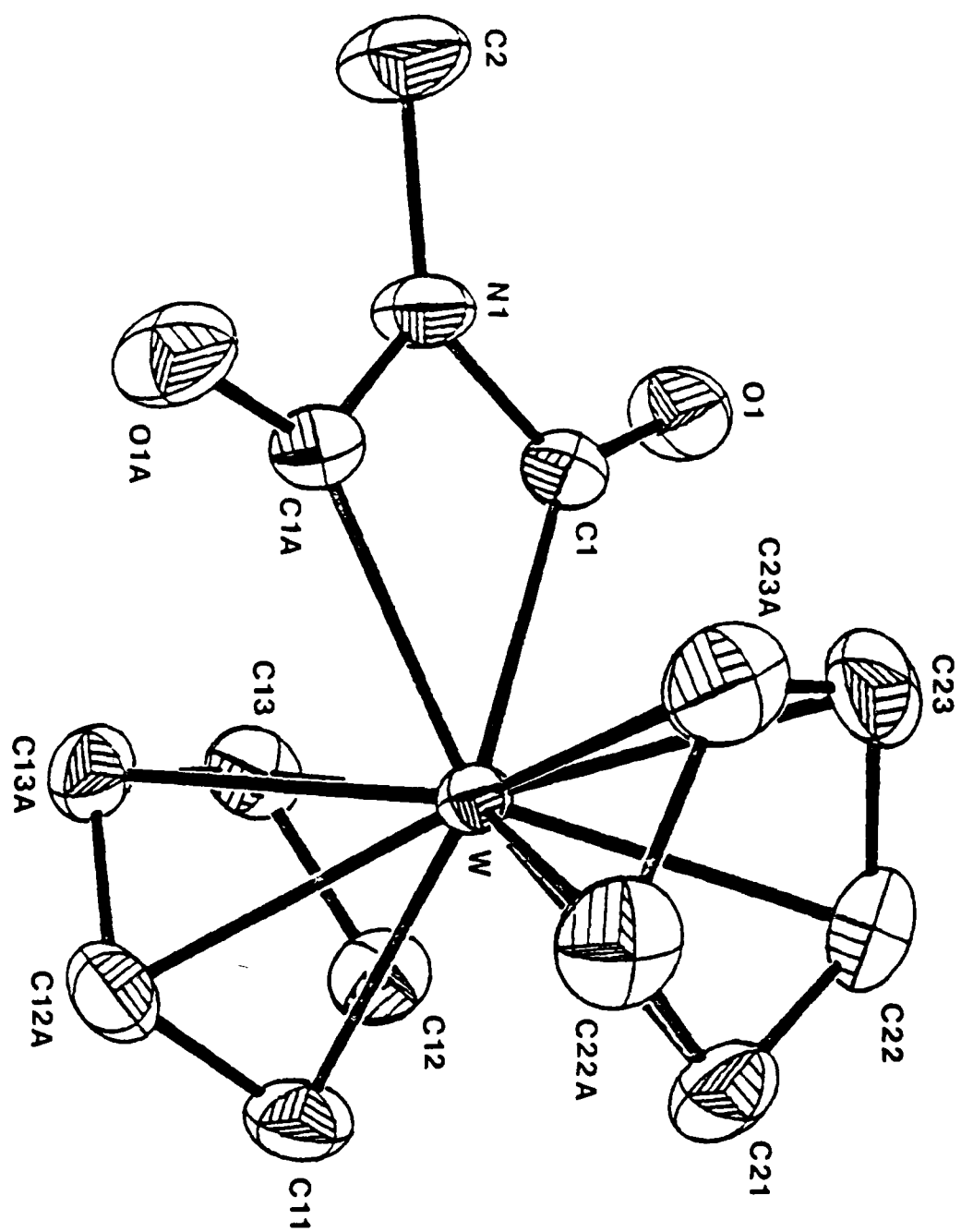
W-C(1) 2.218 (11)	C(11)-C(12) 1.419 (17)	C(31)-C(32) 1.388 (16)
W-C(2) 2.184 (10)	C(12)-C(13) 1.414 (17)	C(32)-C(33) 1.368 (18)
W-C(11) 2.242 (11)	C(13)-C(14) 1.397 (19)	C(33)-C(34) 1.368 (20)
W-C(12) 2.271 (11)	C(14)-C(15) 1.399 (17)	C(34)-C(35) 1.375 (20)
W-C(13) 2.326 (11)	C(15)-C(11) 1.397 (19)	C(35)-C(36) 1.395 (17)
W-C(14) 2.364 (12)	C(21)-C(22) 1.444 (17)	C(36)-C(31) 1.403 (16)
W-C(15) 2.272 (12)	C(22)-C(23) 1.398 (18)	C(41)-C(42) 1.377 (15)
W-C(21) 2.250 (11)	C(23)-C(24) 1.401 (18)	C(42)-C(43) 1.394 (20)
W-C(22) 2.300 (10)	C(24)-C(25) 1.403 (18)	C(43)-C(44) 1.376 (22)
W-C(23) 2.353 (11)	C(25)-C(21) 1.422 (16)	C(44)-C(45) 1.351 (23)
W-C(24) 2.315 (12)		C(45)-C(46) 1.394 (19)
W-C(25) 2.242 (12)		C(46)-C(41) 1.355 (15)
C(1)-S(1) 1.612 (12)	C(1)-N(1) 1.393 (14)	C(2)-N(1) 1.416 (13)
C(2)-N(2) 1.282 (13)	N(2)-C(31) 1.387 (13)	N(1)-C(41) 1.443 (13)

<sup>a</sup>See Figure 2 for atom designations.

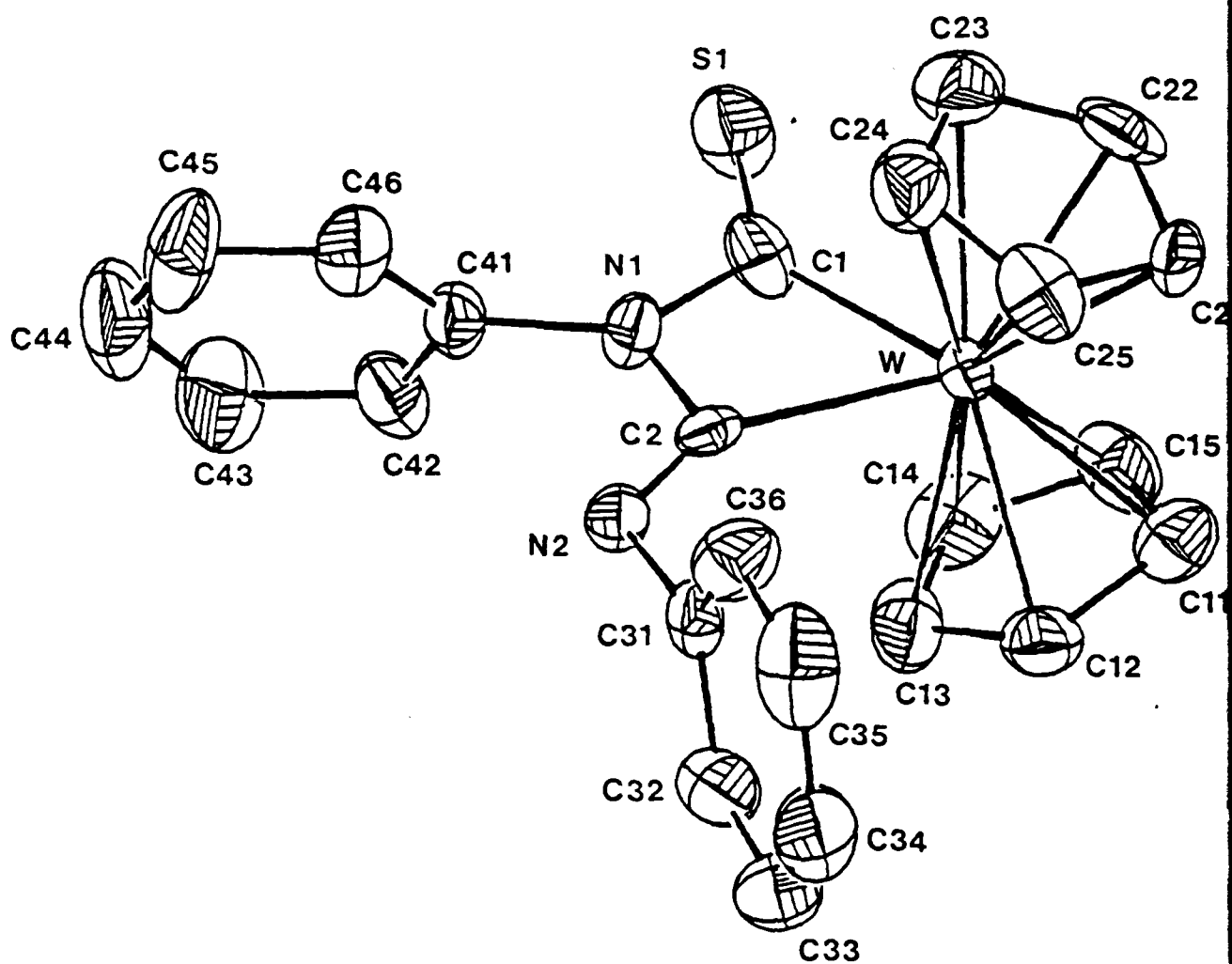
Table VII. Bond Angles (deg) within  $[W(\eta-C_5H_5)_2\{C(S)N(Ph)C(NPh)\}]^a$

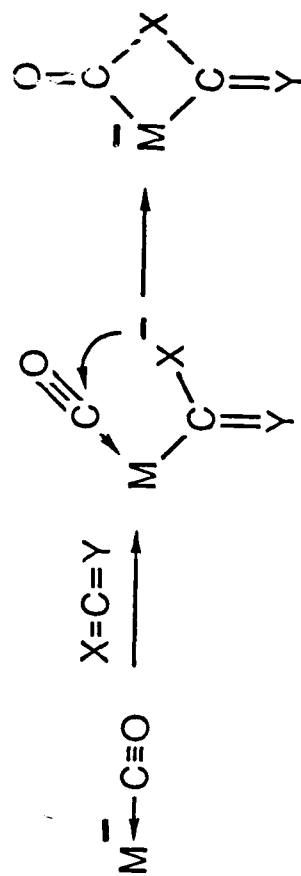
C(1)-W-C(2)	61.9 (4)	C(31)-C(32)-C(33)	122.8 (11)
W-C(1)-S(1)	139.4 (6)	C(32)-C(33)-C(34)	120.3 (12)
W-C(2)-N(2)	144.9 (7)	C(33)-C(34)-C(35)	119.4 (12)
W-C(1)-N(1)	95.0 (7)	C(34)-C(35)-C(36)	120.3 (13)
W-C(2)-N(1)	95.7 (6)	C(35)-C(36)-C(31)	121.0 (11)
C(1)-N(1)-C(2)	107.4 (8)	C(36)-C(31)-C(32)	116.2 (10)
N(1)-C(1)-S(1)	125.6 (8)	C(41)-C(42)-C(43)	118.4 (11)
N(2)-C(2)-N(1)	119.4 (9)	C(42)-C(43)-C(44)	120.9 (13)
C(2)-N(1)-C(41)	125.7 (8)	C(43)-C(44)-C(45)	119.6 (14)
C(1)-N(1)-C(41)	126.8 (9)	C(44)-C(45)-C(46)	120.1 (13)
C(2)-N(2)-C(31)	118.4 (9)	C(45)-C(46)-C(41)	120.4 (12)
N(2)-C(31)-C(32)	121.7 (10)	C(46)-C(41)-C(42)	120.5 (11)
N(2)-C(31)-C(36)	121.6 (9)		
N(1)-C(41)-C(42)	118.3 (9)		
N(1)-C(41)-C(46)	120.9 (10)		
C(11)-C(12)-C(13)	107.4 (11)		
C(12)-C(13)-C(14)	108.7 (10)		
C(13)-C(14)-C(15)	107.2 (12)		
C(14)-C(15)-C(11)	109.7 (12)		
C(15)-C(11)-C(12)	107.1 (11)		
C(21)-C(22)-C(23)	107.8 (11)		
C(22)-C(23)-C(24)	108.2 (11)		
C(23)-C(24)-C(25)	109.4 (11)		
C(24)-C(25)-C(21)	107.5 (11)		
C(25)-C(21)-C(22)	107.0 (10)		

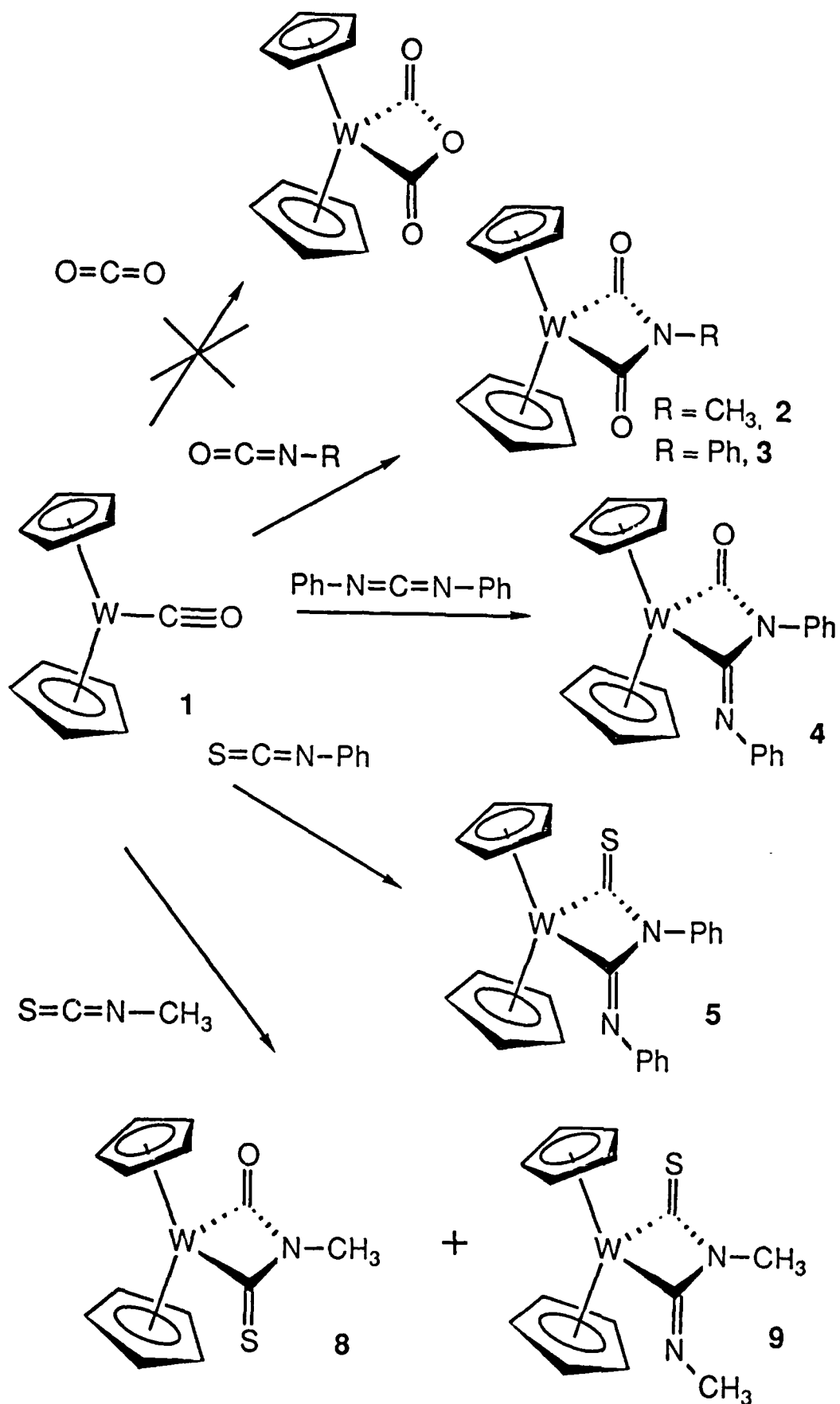
<sup>a</sup>See Figure 2 for atom designations.



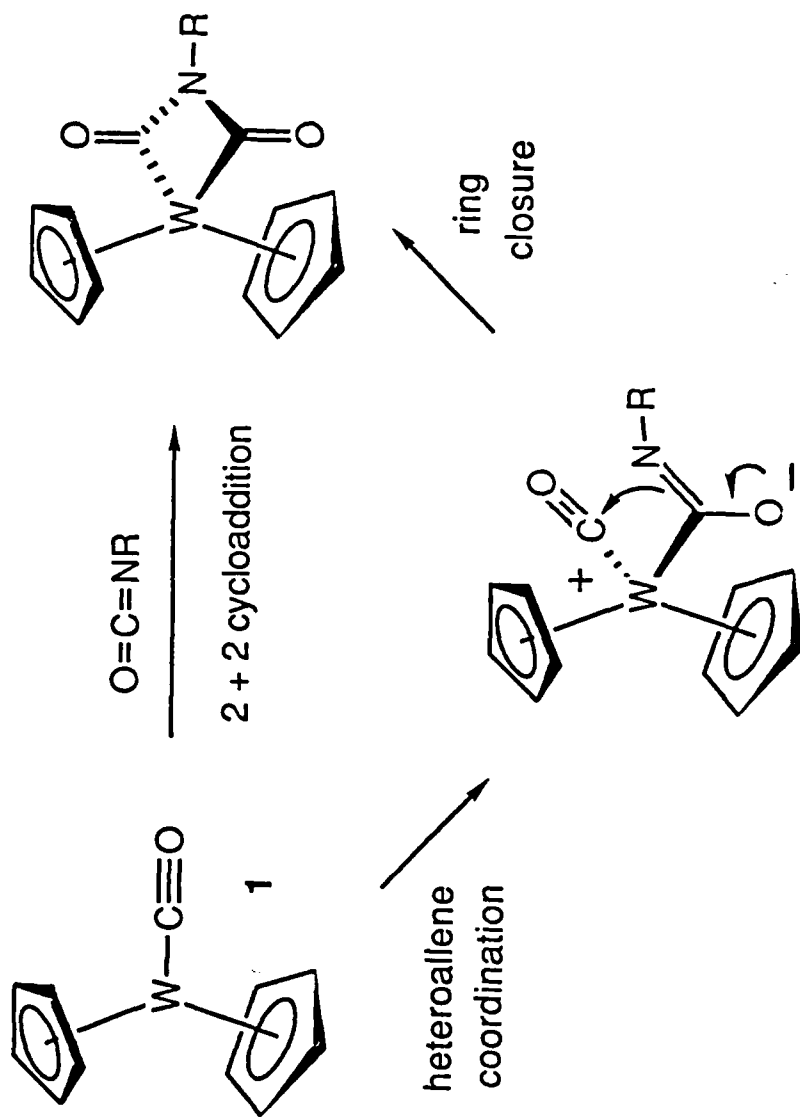




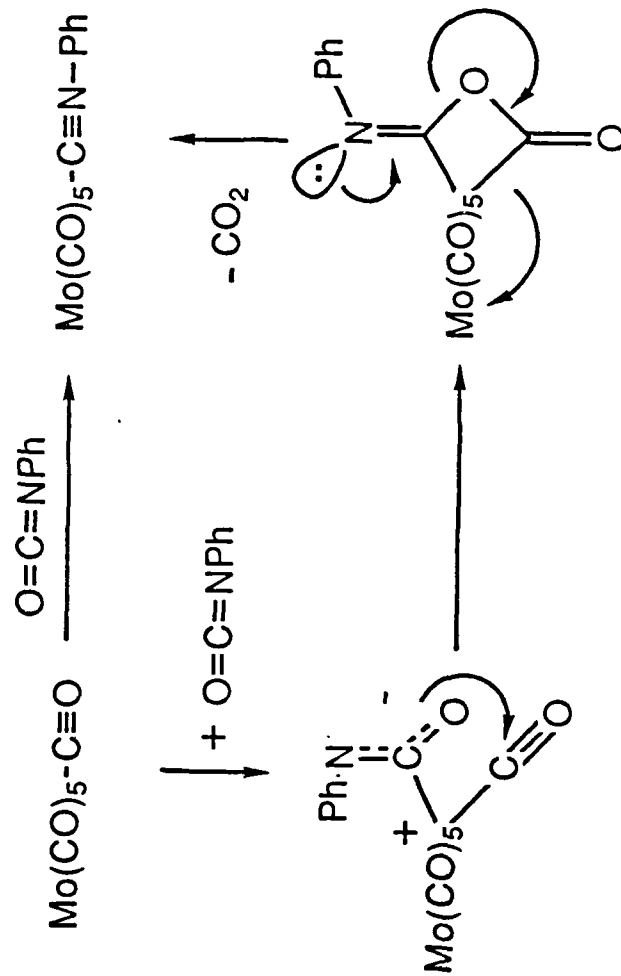




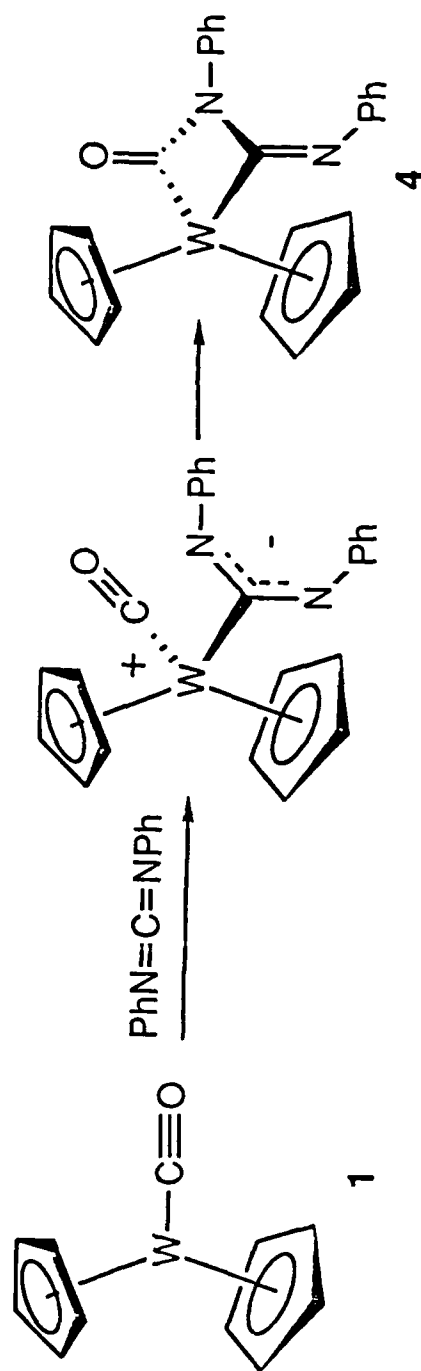
Scheme I. Products of Heteroallene Addition to  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ .



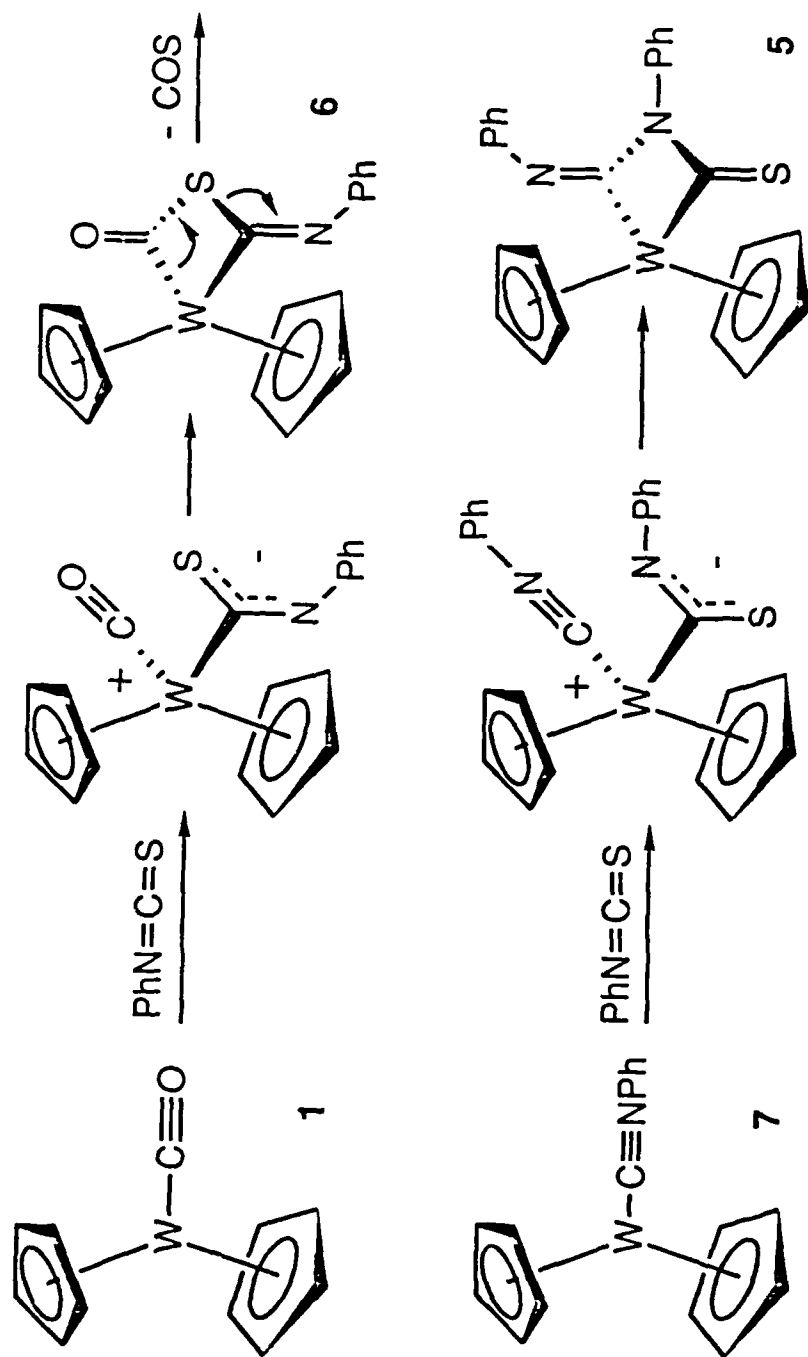
Scheme II. Possible Mechanism for Macrocyclic Complex Formation



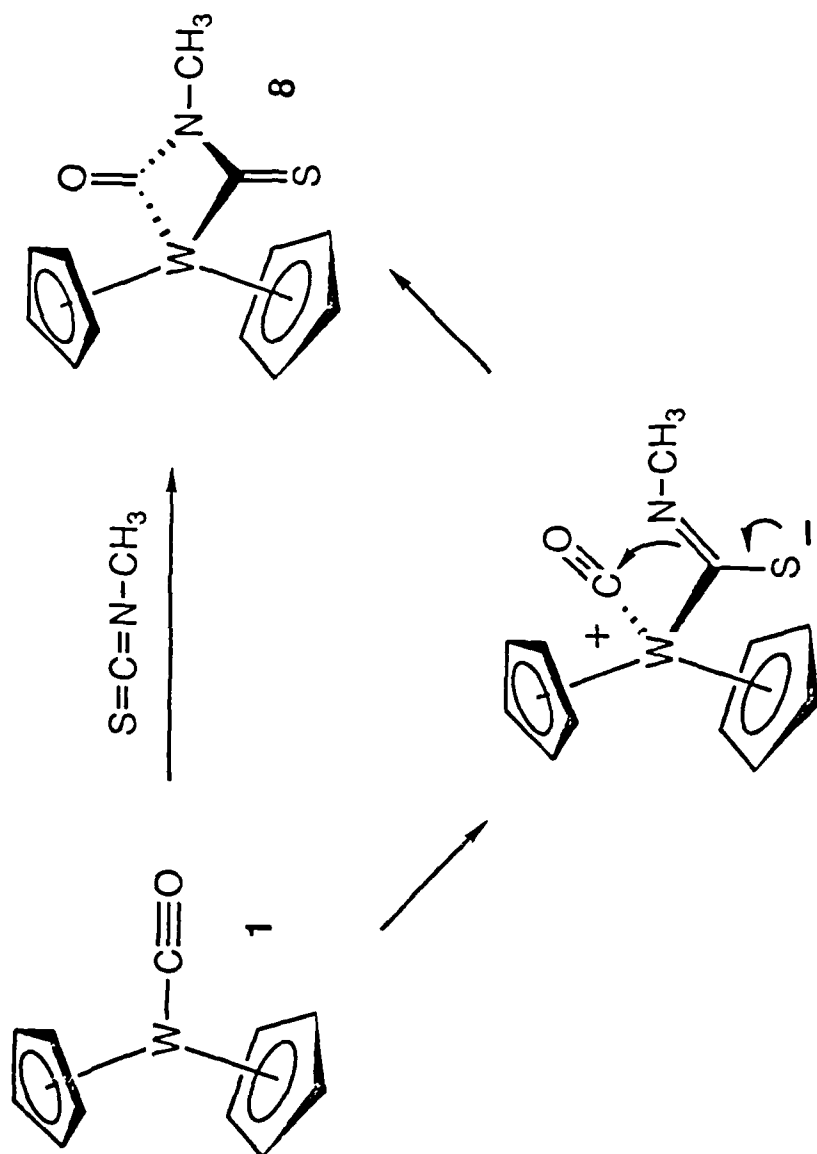
Scheme III. Probable Mechanism for the Formation of an Isocyanide Ligand by Addition of an Isocyanate to  $[\text{Mo(CO)}_6]$ .



Scheme IV. Proposed Mechanism for the Formation of **4**.



Scheme V. Proposed Mechanism for the Formation of 5.



Scheme VI. Proposed Mechanism for the Formation of 8.



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